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To aid in the development of boron-enhanced fluorinitramino explosives, the kinetics of individual reactions are measured over wide temperature ranges. It is found that the pre-exponentials of rate coefficients of BO reactions tend to be two orders of magnitude smaller than for the AlO reactions with the same oxidants. This may explain why no reaction could be observed between BO and CO_2, $k < 1 \times 10^{-14}$ cm^3 molecule^{-1}s^{-1}.

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PROGRESS

Introduction

The goals of this program are:

(i) to make accurate measurements, over wide temperature ranges, of rate coefficients for boron combustion in C/H/N/O/F environments, needed for models used in the development of new underwater explosives, and

(ii) to use the measurements to obtain a further understanding, to allow predictions for additional reactions occurring with such explosives.

To this end measurements are made in unique high temperature reactors of the HTFFR (high-temperature fast-flow reactor) and HTP (high-temperature photochemistry) type. These are to be supplemented, where warranted, by semi-empirical and *ab initio* studies.

Results

A series of measurements have now been made on BO reactions. The remarkable observation is that the pre-exponentials of the rate coefficients are much lower than for the corresponding AlO reactions. Witness the following two pairs, where the rate coefficients are expressed in cm^3 $molecule^{-1}$ s^{-1} units:

(1) $BO + O_2 \rightarrow BO_2 + O$; $k(300\text{-}1000\ K) = 7.9\times10^{-12}\exp(161\ K/T)$ (Ref. 1)

(2) $AlO + O_2 \rightarrow AlO_2 + O$; $k(1200\text{-}1690\ K) = 7.7\times10^{-10}\exp(-10008\ K/T)$ (Ref. 2)

(3) $BO + HCl \rightarrow (HBO + Cl)$ and/or $(OBCl + H)$; (Ref. 1)
$k(300\text{-}760\ K) = 6.3\times10^{-13}\exp(-1403\ K/T)$

(4) $AlO + HCl \rightarrow (HAlO + Cl)$ and/or $(OAlCl + H)$; (Ref. 3)
$k\ (440\text{-}1590\ K) = 5.6\times10^{-11}\ \exp\ (-139\ K/T)$

The exothermic $BO + CO_2 \rightarrow BO_2 + CO$ reaction (5) was found to be immeasurably slow,[1] $k\ (300\text{-}1200\ K) < 3\times10^{-14}$. The $AlO + CO_2$ reaction, proceeded with k about 4×10^{-14} in this temperature range.[4] An *ab initio* study of reaction (5) showed evidence for a $BOCO_2$ adduct, but no barrier.[5] Hence, a small pre-exponential should be the cause of the small k(5). Current boron combustion models are very sensitive to this reaction.

PLANS

Further experimental studies planned include the reactions of BO with N_2O, and HF, and of BF with BF_3, O_2 and H_2O.

The reason for the above-noted differences in the pre-exponential parts of the rate coefficients of the monoxides of the two group 13 elements B and Al is being considered. In previous work from this laboratory much smaller differences between BCl and AlCl rate coefficients were observed.[6,7,8] The BCl reactions with O_2 and CO_2 are actually somewhat faster than their AlCl counterparts. For N_2O the reverse relation holds. Semi-empirical SECI theory was applied successfully to predict the relation between the exponential terms for a series of those reactions.[9] This approach might be extended to the monoxides. These combined considerations are significant for allowing predictions of k(T) values, in addition to those measured, with greater accuracy than appears in the current literature for such refractory species reactions.

PARTICIPANTS AND CONTACTS

The principal participant on this project was J.-D.R. Rocha, an MS/Ph.D. student.

PUBLICATIONS AND AWARDS

1. D.P. Belyung, G.T. Dalakos, Q. Zhang, J.D.-.R. Rocha, and Fontijn A., "Wide Temperature Range Studies of BO and BO_2 Reactions", Abstract for The Fourth International Conference on Chemical Kinetics at NIST, July 1997. A full-length paper by the same title is in preparation.

There were no Awards this year.

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7. P.M. Futerko and A. Fontijn, "Experimental and Transition-State Theory Studies of the Gas-Phase Reactions of AlCl with N_2O, CO_2, and SO_2", J. Phys. Chem. 97, 7222 (1993).

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